AI-64-240

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13 June - 13 September 1964
Prepared for Jet Propulsion Laboratory
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by

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SUMMARY

Experimental results on the loss of capacity of the cadmium electrode in a Co-60 radiation field exhibited much scatter although the corresponding blank runs at similar temperature (45°C) outside the radiation field gave more uniform results. The cadmium electrodes of Ni-Cd cells with a single compartment lost about 15 per cent of their ampere hour capacity at 75 per cent of charge during a Co-60 gamma irradiation of $8.9 \pm 0.2 \times 10^7$ rads (H_2O). Under the same conditions, and with the same dose, at 100 per cent and 50 per cent of full capacity, little loss in capacity was observed.

Limited data to date on the amount of material sloughed from the electrodes as a function of state of charge would seem to indicate that less material is lost at 50 per cent of charge than at either 75 or 100 per cent. Also, the Cd/Ni ratio is lower at 50 per cent of charge than at 100 per cent. From data on two runs, in which the electrodes were separated by a porous quartz disc, most of the sloughed material at 50 and 75 per cent of charge came from the cadmium electrode.

The radiolytic data indicate that after an irradiation of 6.6×10^7 rads (about 47 hours at 1.4×10^6 rads/hr.) the KOH system is in a steady state condition as far as net production of radiolysis products is concerned. The apparent G values (molecules produced/100 e.v.) for O_2 and H_2 were shown to decrease with increasing KOH concentration in the range 0.5 per cent KOH to 20 per cent KOH, and then to increase at higher concentrations up to 40 per cent KOH. The presence of a nickel electrode was found to cause a 20 fold increase in G_{O_2}, while the cadmium electrode effected a 10 fold increase in G_{H_2}.

Over

Voltammetry experiments on the nickel and cadmium electrodes of a cell before, during and after an irradiation (of 8.9×10^7 rads; dose rate = 1.4×10^6 rads/hr.) showed that little, if any, polarization could be attributed to the effect of the radiation.

I. INTRODUCTION

The purpose of this project is to study the effects of radiation on nickel and cadmium (Ni-Cd) electrodes. A report entitled, "The Effects of Radiation on Ni-Cd Battery Electrodes. I" issued February 6, 1964[1] covers the exploratory studies of these electrodes in neutron, gamma and electron radiation fields. A second report,[2] issued July 29, 1964, describes the studies carried out with gamma radiation (a) to determine the factors affecting the observed loss in capacity of the cadmium electrode, and (b) to investigate the radiolysis of various concentrations of KOH.

The present report discusses work on (a) the radiation induced loss in capacity of the cadmium electrode, (b) the origin of the sloughed electrode material, (c) the radiolysis of aqueous KOH solutions, and (d) the current-voltage characteristics of the nickel and cadmium electrodes in a radiation field.

II. EXPERIMENTAL

A. Cadmium Electrode Capacity Studies

Electrodes from Gulton type VO .8 Ni-Cd cells (manufactured by the Alkaline Battery Division, Gulton Industries, Inc.) were used for the study. In a cell consisting of one nickel and one cadmium electrode, the nickel electrode is normally the ampere hour capacity limiting electrode. Since it has been observed that the capacity of the cadmium electrode was reduced by irradiation, it was desired to make the cadmium electrode limit the cell capacity. This was done by physically cutting off one-third of the cadmium electrode with a sharp paper cutter and using only two-thirds of it in the cell.

Measurement of the ampere hour capacity of the cadmium electrode proceeded as described previously[2] using a constant current of 0.20 amperes for all charge and discharge cycles. (This corresponds to a rate of $\frac{C}{2}$.) This capacity was determined as the time it took a fully charged cell to drop 0.2 volt below the relatively flat portion of the discharge curve. At least three measurements of capacity were made before and after each irradiation, and before and after each elevated temperature (45°C) blank run. These blank runs were used as a reference for all irradiation runs. From measurements reported earlier,[2] the state of charge of these electrodes appeared to be a likely parameter in this observed capacity loss. Several runs were made at 100, 75 and 50 per cent of full charge to determine this effect.

These capacity studies presented an opportunity to study the amount of material sloughed from the electrodes as a function of state of charge. In addition to the amount of material lost, the electrode from which the material came could also be determined. To accomplish the latter, a porous quartz disc was used to divide the cell into nickel and cadmium compartments. The Hg/HgO/KOH reference electrode was placed in the cadmium compartment so that the magnitude of the IR drop would be minimal to the cadmium electrode, the one of particular interest for the loss of capacity study. This cell is shown in Figure 1. The capacity was measured as indicated previously.[2] After the post-irradiation measurements of capacity, the cell was opened and the contents of each compartment were removed separately. Each solution was then filtered and the residues dried, weighed and analyzed for cadmium to nickel ratio by the x-ray fluorescence method. Emission spectrographic analysis in many cases was used to check these ratios, and to give a more complete analysis of the residue. X-ray diffraction was also used on three samples to determine which compounds of nickel and cadmium were present.

B. Radiolysis Studies

Experimental conditions for these studies were about the same as those reported previously.[2] In summary, these runs were carried out by sealing a 10 ml sample of the KOH solution in a quartz tube of about 20 ml capacity under a helium atmosphere, and placing these tubes into the radiation field.

Since the volumes of gas produced by radiolysis from these (and previous) samples were small, a new, smaller, gas sampling system was used

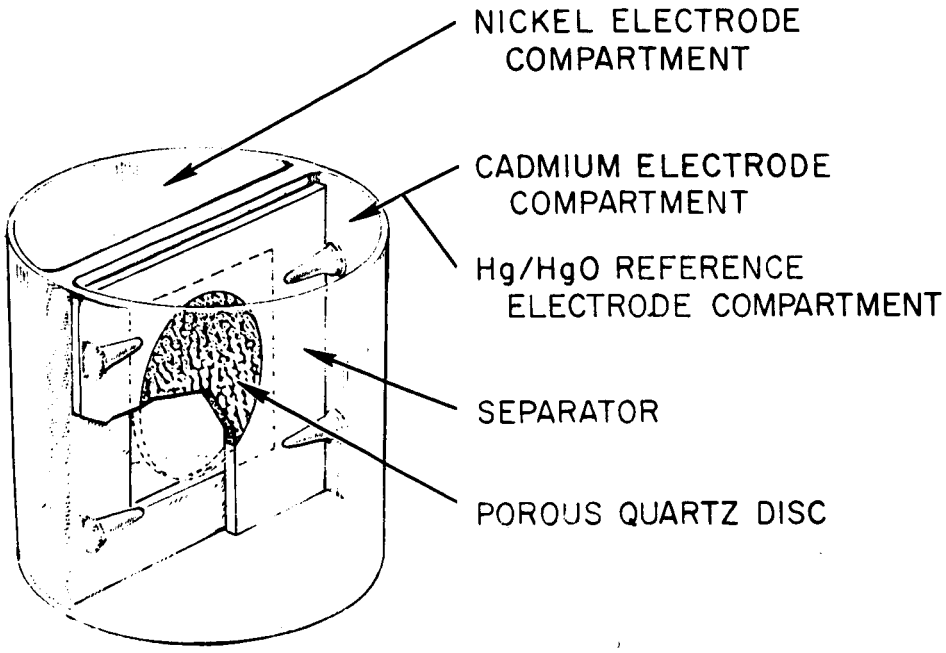

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Figure 1. Quartz Cell Liner with Porous Quartz Separator

with the gas chromatograph to increase the accuracy of the measurements. The new system is shown in Figure 2. The large sample volume system used earlier was separated from the smaller volume system by a stopcock and could be switched into the overall system if large gas samples were encountered.

C. Voltammetry Studies

Fast sweep voltammetry was chosen as the best method for studying polarization effects at the nickel and cadmium electrodes caused by gamma radiation. The cell using a quartz liner in the stainless steel case, as described previously,[2] was used for this study. An Anotrol Potential Controller Model No. 4100, having current capabilities of 15 amperes anodic and 2.5 amperes cathodic was used for the voltage sweeps. This instrument could sweep between any preset voltages in 0.5 second. A Tektronix Oscilloscope, Model No. 561A, with Polaroid camera attachment was used to record current and voltage data during these fast sweeps. The current capabilities of the potential controller, although quite high for this type of instrument, were too low to polarize entire nickel or cadmium electrodes. Therefore, the electrodes were cut to one-fourth of their original size to reduce the effective electrode area by this factor so that they could be polarized at the available currents.

Experiments were carried out in the laboratory to determine the conditions required to polarize these particular electrodes. The voltage chosen for the start of all the sweeps was the rest potential between the reference (Hg/HgO) electrode and the electrode in question, either the

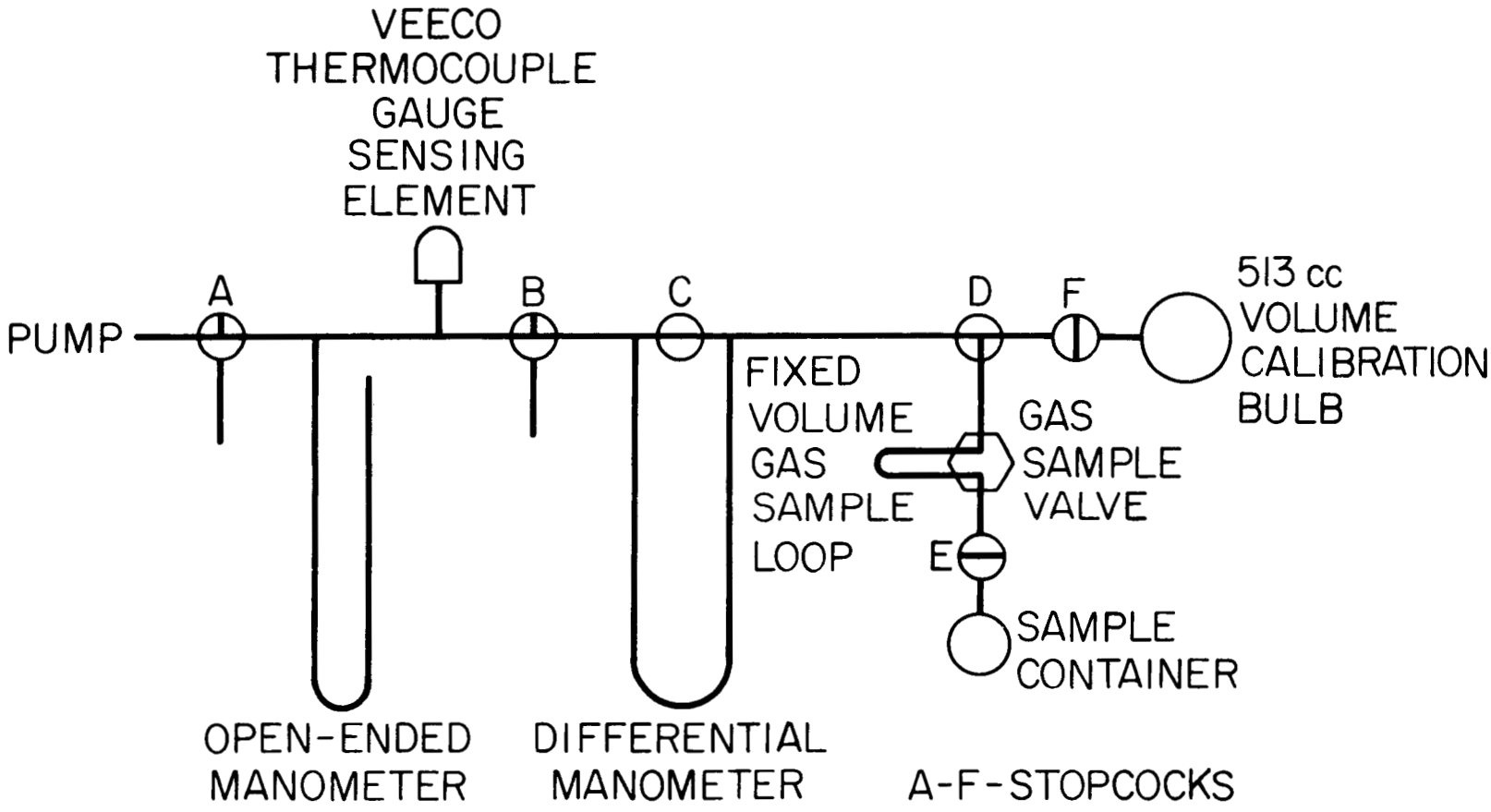

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Figure 2. Schematic of System for Radiolytically Produced Gas Sample Analysis

nickel or cadmium. This starting voltage varied somewhat as the runs progressed so measurement of this voltage was required before each run. The magnitude of the Cd-Hg/HgO voltage was about 0.80 volt while that of the Ni-Hg/HgO voltage was close to 0.40 volt.

III. RESULTS

A. Cadmium Electrode Capacity

The results of the cadmium electrode capacity experiments are summarized in Tables I.A., I.B. and II. Table I.A. gives the results obtained with single compartment irradiated cells; Table I.B. gives the results obtained with two compartment irradiated cells (each electrode in a separate compartment). Table II gives results from blank runs at 45°C; those runs with the same A- number correspond and were run simultaneously.

TABLE I.A. RESULTS OF CADMIUM ELECTRODE CAPACITY EXPERIMENTS WITH SINGLE COMPARTMENT IRRADIATED* CELLS

Run #	% of Full Charge	Charge (Min. @ 0.2 amp)	Initial Capacity (Min. @ 0.2 amp)	Final Capacity (Min. @ 0.2 amp)	% Change
A-2-R	100	110	93	88	- 5.4
A-11-R	100	120	106	111	+ 4.7
A-14-R	100	120	98	91	- 7.1
A-1-R	75	150	134	112	-16.4
A-3-R	75	110	107	92	-14.0
A-9-R	50	120	104	100	- 3.8
A-12-R	50	120	103	103	0

*Total γ dose for these runs was $8.9 \pm 0.2 \times 10^7$ rads.

TABLE I.B. RESULTS OF CADMIUM ELECTRODE CAPACITY EXPERIMENTS WITH TWO COMPARTMENT IRRADIATED* CELLS

Run #	% of Full Charge	Charge (Min. @ 0.2 amp)	Initial Capacity (Min. @ 0.2 amp)	Final Capacity (Min. @ 0.2 amp)	% Change
A-5-R	100	110	96	86	-10.4
A-13-R	75	120	104	97	- 6.7
A-7-R	50	120	82	96	+17.1

*Total γ dose for these runs was $8.9 \pm 0.2 \times 10^7$ rads.

TABLE II. RESULTS OF CADMIUM ELECTRODE CAPACITY EXPERIMENTS 45°C BATH RUNS*

Run #	% of Full Charge	Charge (Min. @ 0.2 amp)	Initial Capacity (Min. @ 0.2 amp)	Final Capacity (Min. @ 0.2 amp)	% Change
A-2-B	100	110	98	93	- 5.1
A-5-B	100	110	100	102	+ 2.0
A-11-B	100	120	102	100	- 2.0
A-14-B	100	120	103	103	0
A-4-B	75	110	99	97	- 2.0
A-13-B	75	120	101	99	- 2.0
A-6-B	50	110	105	102	- 2.9
A-7-B	50	120	110	115	+ 4.5
A-12-B**	50	120	96	94	- 1.9

*45°C is the temperature attained by all cells undergoing irradiation in Co-60 source.

**Run made in compartmented cell.

The results from single and double compartment irradiated cells were listed separately, as there may be differences in the effects of radiation

in these configurations. That is, the radiolysis product environment of each isolated electrode in a cell undergoing irradiation may differ from that when it is near the other cell electrode. Actually, while the data are few, this does seem to be the case.

These results indicate that, with the single compartment cells at least, a significant capacity loss occurs in an irradiated cell at 75 per cent of charge, while little if any loss occurs at 100 per cent and 50 per cent of charge.

A plot of change of capacity of the cadmium electrode for runs in unchambered cells as a function of state of charge is shown in Figure 3. The unirradiated cell data in Table II indicate that temperature has little effect if any on the capacity of the cadmium electrode.

B. Weight and Analyses of Sloughed Material

Material was observed to be sloughed off the nickel and cadmium electrodes during Co-60 gamma irradiations.[1] Indirect evidence had indicated that at 75 per cent of full charge most of the material came from the nickel electrode.[1] The experiments carried out during the present period were designed (a) to obtain more direct evidence as to the source of the sloughed material and (b) to determine how the sloughing was affected by the state of charge of the electrodes. The data obtained are shown in Table III. Additional data are needed to make the picture complete.

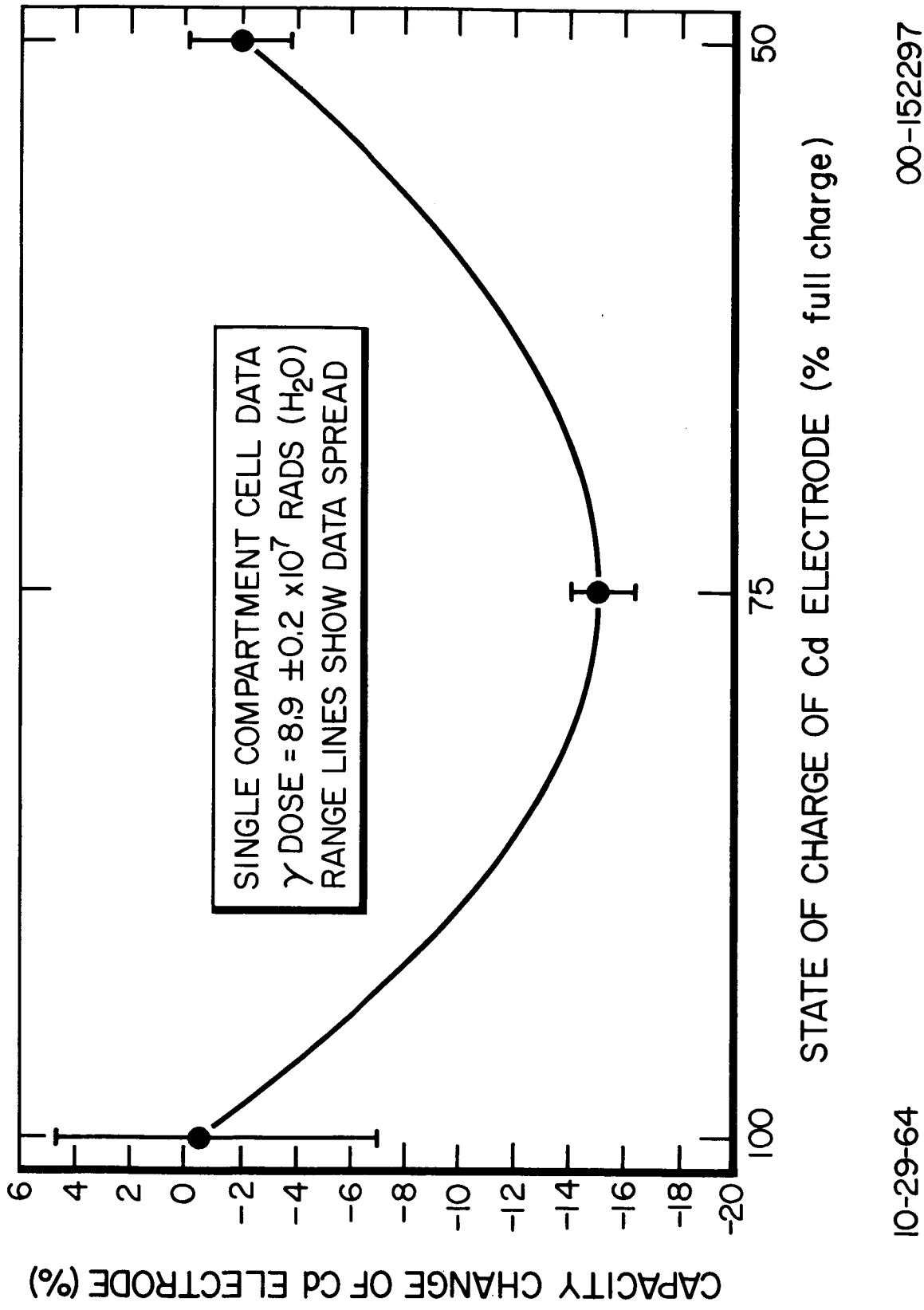

Figure 3. Capacity Losses of Cd Electrode as a Function of State of Charge

TABLE III. EFFECT OF STATE OF CHARGE ON WEIGHT LOSS FROM ELECTRODES

(Dose on Irradiated Cells = 8.9 ± 0.2 x 10^7 rads)

Run #	State of Charge	Total Weight Loss from Both Electrodes (mg)		Cd/Ni Ratio of Material from Undivided Cell	Amt. Lost[4] from Nickel Electrode (mg)	Cd/Ni Ratio: Material in Nickel Compartment	Amt. Lost[4] from Cadmium Electrode (mg)	Cd/Ni Ratio: Material in Cadmium Compartment
		Irradiated Cell	45°C Reference Cell					
A-2[2]	100	16.9	4.0	20:1	---	---	---	---
A-5[4]	100	41.8	---	---				
A-10	100	27.4	4.0	10:1				
A-11	100	19.6	4.6	10:1				
A-1[2,3]	75	26.7		30:1				
A-13[4]	75	16.7	5.2		2.0	1:1	14.7	16:1
Co-60 #2[5,6]	75	35.6		6:1				
Co-60 #3[5]	75	10.1		7:1				
A-7[4]	50	15.2	6.0[1]	5:3	3.5	1:1	11.7	5:3
A-9	50	3.3		5:1				
A-12	50	14.0	5.6	6:1				

(1) Contaminated with Hg and HgO from reference electrode

(2) X-ray analysis shows $Cd(OH)_2$ + Cd metal + SiO_2. The $Cd:Cd(OH)_2$ ratio higher in A-2 than in A-1

(3) Cell had two nickel and one cadmium electrode

(4) Compartmented cell

(5) Data previously reported in AI-64-11[1]

(6) Dosage = 1.0 x 10^8 rads

C. Radiolysis of KOH Solutions

Various concentrations of aqueous KOH were irradiated in a Co-60 source to determine the products produced, the quantity of each, and the effect of the materials from the nickel and cadmium electrodes on this production. Hydrogen and oxygen were the only products detected. No hydrogen peroxide (less than 1 μg/cc) was detected in any of the samples examined approximately 24 hours after removal from the field. "G" values for the production of these gases were calculated. (The "G" value is defined as the number of molecules produced per 100 ev of radiation.) The data from these studies are given in Table IV. "G" values for H_2 and O_2 in 30 per cent KOH in the presence of nickel or cadmium electrodes were also obtained and are shown in Table V. These data are represented graphically in Figure 4.

TABLE IV. RADIOLYSIS PRODUCTS AND CALCULATED YIELDS FROM CO-60 GAMMA IRRADIATION OF VARIOUS CONCENTRATIONS OF KOH

(Dose = 6.6×10^7 rads; Temp. = 45°C; He Cover Gas)

Run #	% KOH	Gas Phase Composition			Sample System* Pressure (mm Hg)	$G_{(H_2)}$	$G_{(O_2)}$
		% H_2	% O_2	% N_2			
R-8-9	0.5	22.4	12.0	0.04	56	0.09	0.05
R-10-2	0.5	11.4	7.7	.84	74	0.07	0.04
R-10-3	0.5	19.1	9.2	.85	44	0.07	0.03
R-6-1	10	2.2	0	0.34	22	.038	0
R-8-F	10	0.8	0.16	0.30	19	.012	0
R-6-2	20	5.9	0	0.31	28	.014	0
R-6-3	20	3.5	0	0.77	28	.009	0
R-8-C	30	2.0	0.8	4.0	39	0.008	0.002
R-8-D	30	4.1	1.5	4.1	19	0.008	0.002
R-8-2	40	5.9	2.0	0.2	21	0.009	0.003
R-6-4	40	16	3.4	5.6	5	0.008	0.009
R-10-4	40	5.3	1.9	1.5	39	0.01	0.005

* Sample system pressure measured when cell connected to chromatographic sampling system. Variations in this parameter in the runs with He cover gas probably arise from variable expansion of the gas during cell sealing prior to irradiation.

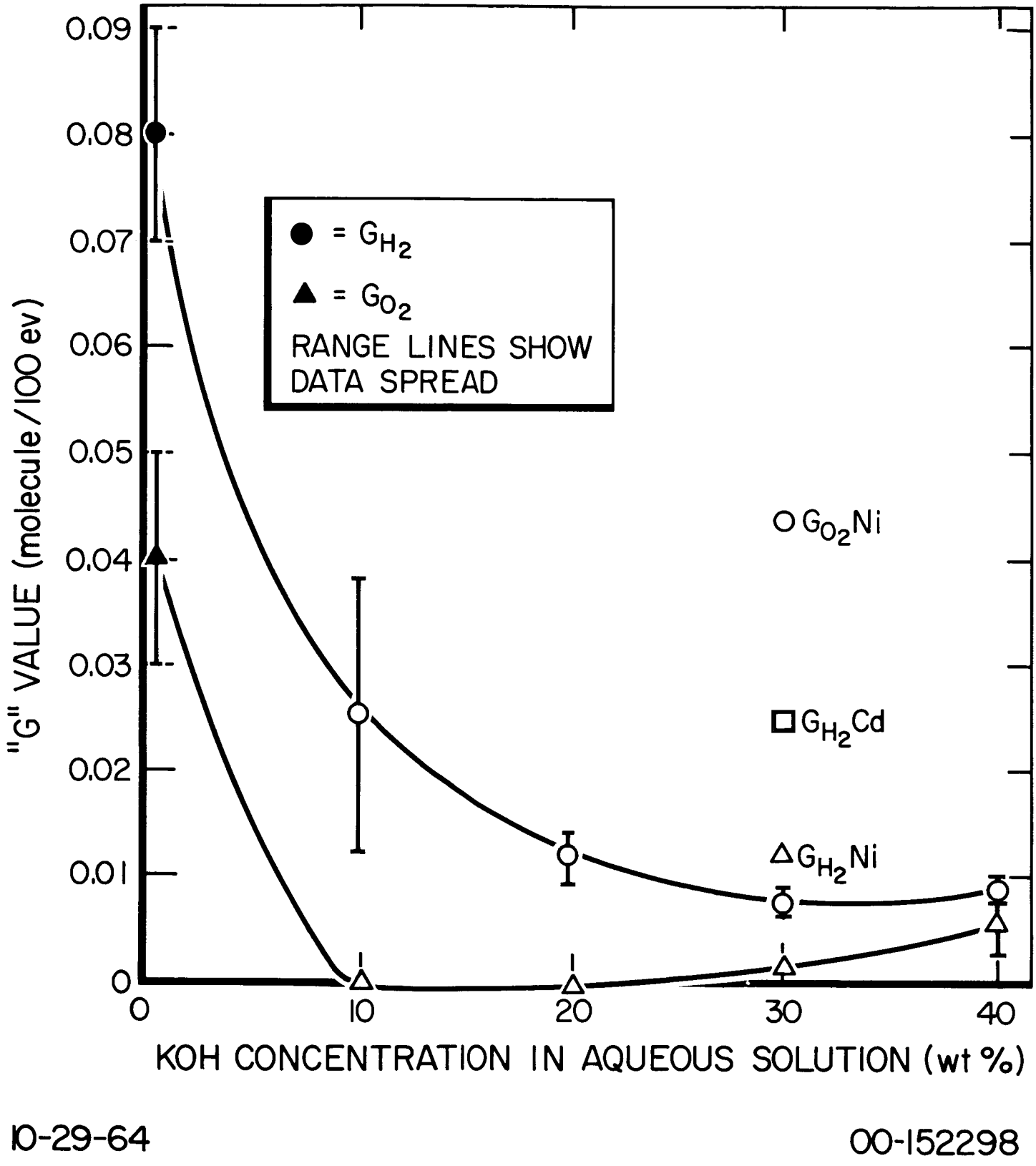

Figure 4. "G" Values for $H_2 + O_2$ as a Function of KOH Concentration

TABLE V. RADIOLYSIS OF 30% KOH CONTAINING Ni or Cd ELECTRODES

(Dose = 6.6×10^7 rads; Temp. = 45°C; He Cover Gas)

Run #	Electrode	Gas Phase Composition % H_2	% O_2	% N_2	Sample System*** Pressure (mm Hg)	$G_{(H_2)}$	$G_{(O_2)}$
R-8-4*	Ni	9.9	52.3	0	16	0.014	0.044
R-10-6	Ni	3.8	25.1	0	27	0.009	0.052
R-8-3	Cd	16.1	0	0.44	21	0.025	0
R-10-5	Cd	6.0	.01	1.2	51	0.025	0
R-8-5**	Ni	0	16.1	1.1	17	—	—

*$G_{(O_2)}$ corrected for apparent self discharge to produce O_2 as observed in R-8-5.

**These samples were not irradiated but rather were stored at 45°C for a period equal to the irradiation time.

***See footnote Table IV.

D. Experimental Voltammetry Data

Fast anodic and cathodic voltage sweeps were made on both the nickel and cadmium electrodes relative to the respective rest potentials, i.e., the voltage of the electrode with reference to the Hg/HgO electrode, at various times before, during and after the irradiation. The data, as shown in Figure 5 and 5A for the nickel electrode and in Figure 6 and 6A for the cadmium electrode, were calculated from the pictures of the voltage sweeps obtained from the oscilloscope. The linear IR drop was subtracted from the voltage in each case. To get the anodic and cathodic data for each case, two pictures were required; these are combined in the calculated figures to show the complete current-voltage characteristics of the electrodes.

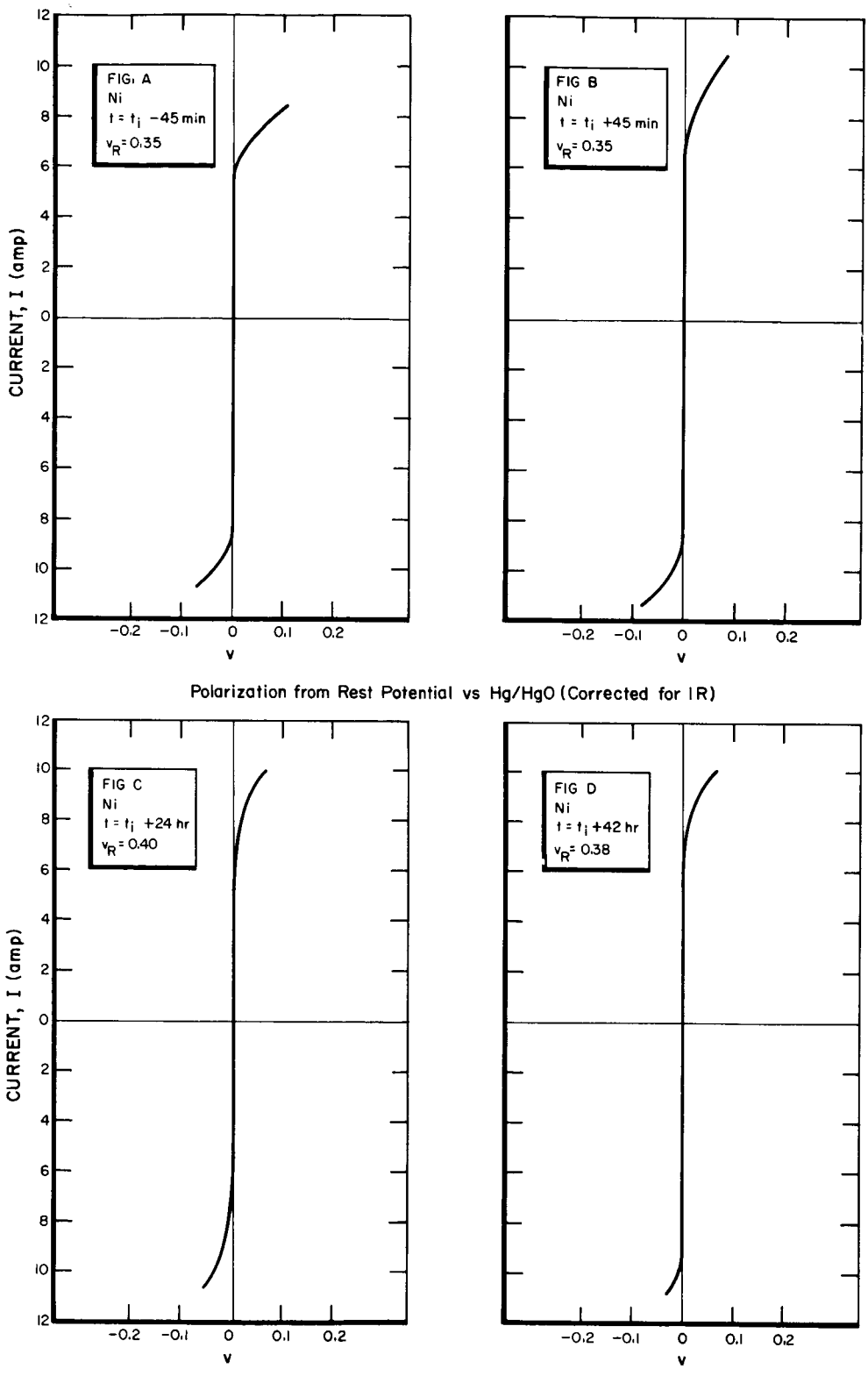

Figure 5. Polarization of Ni Electrode

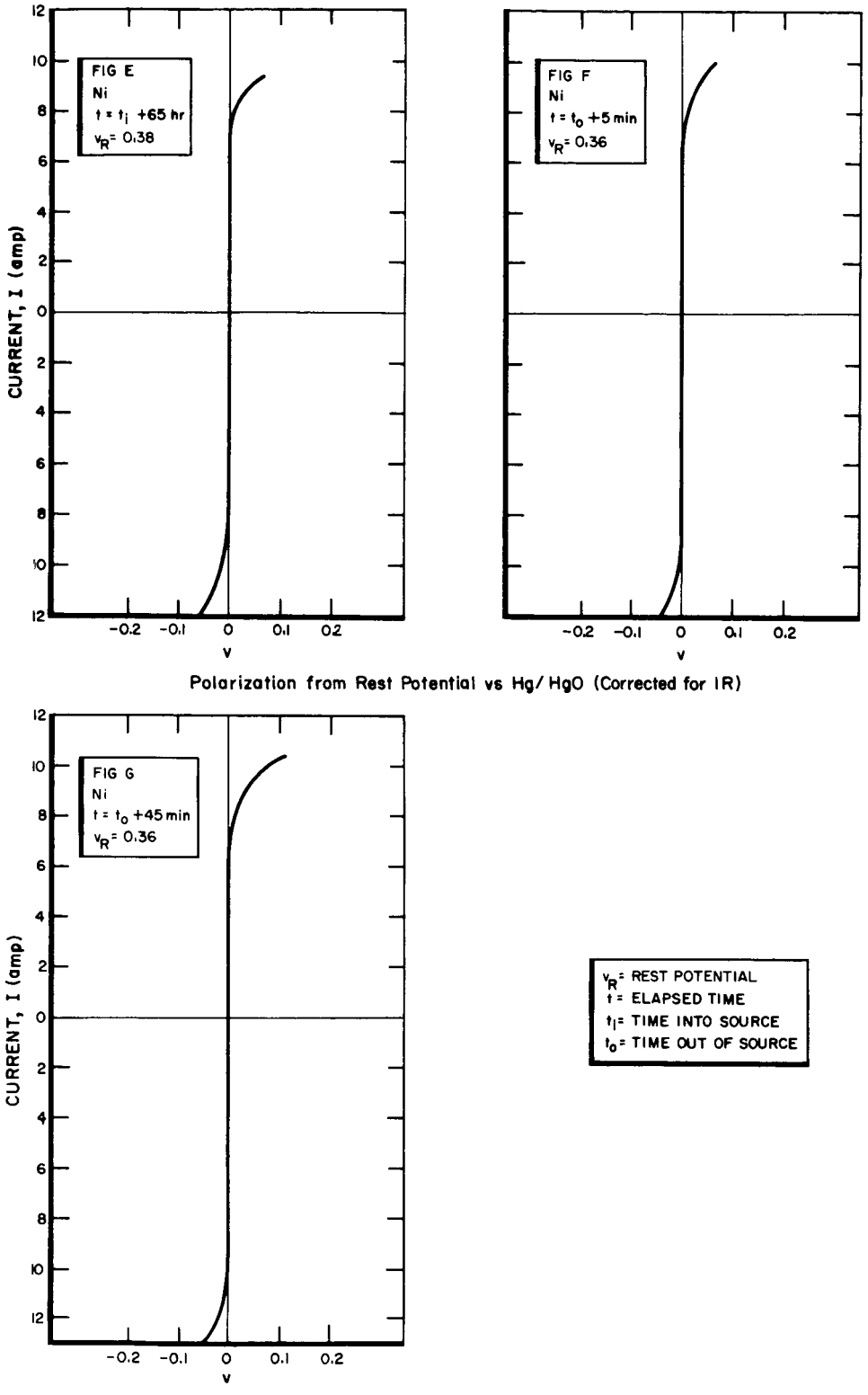

Figure 5A. Polarization of Ni Electrode

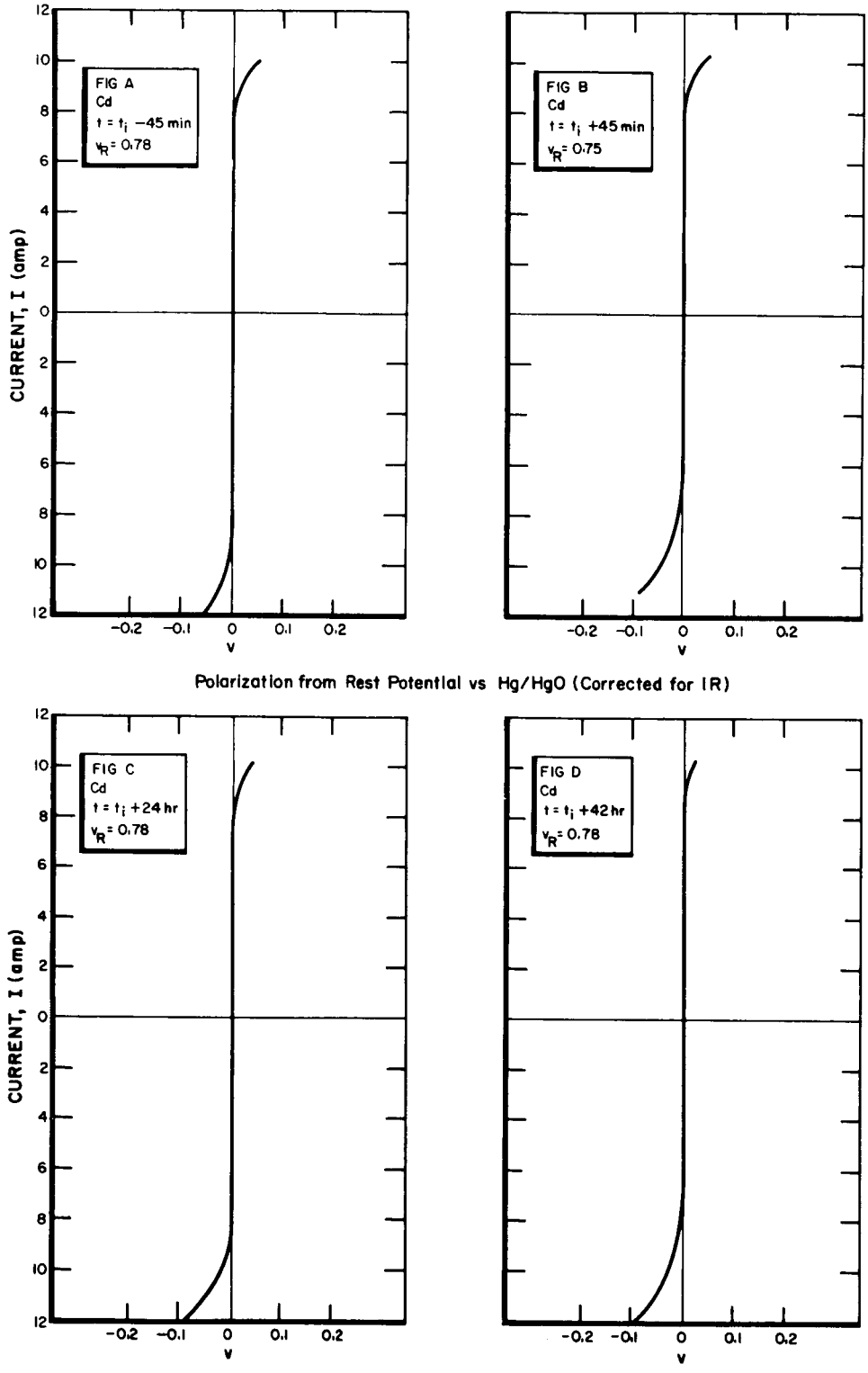

Figure 6. Polarization of Cd Electrode

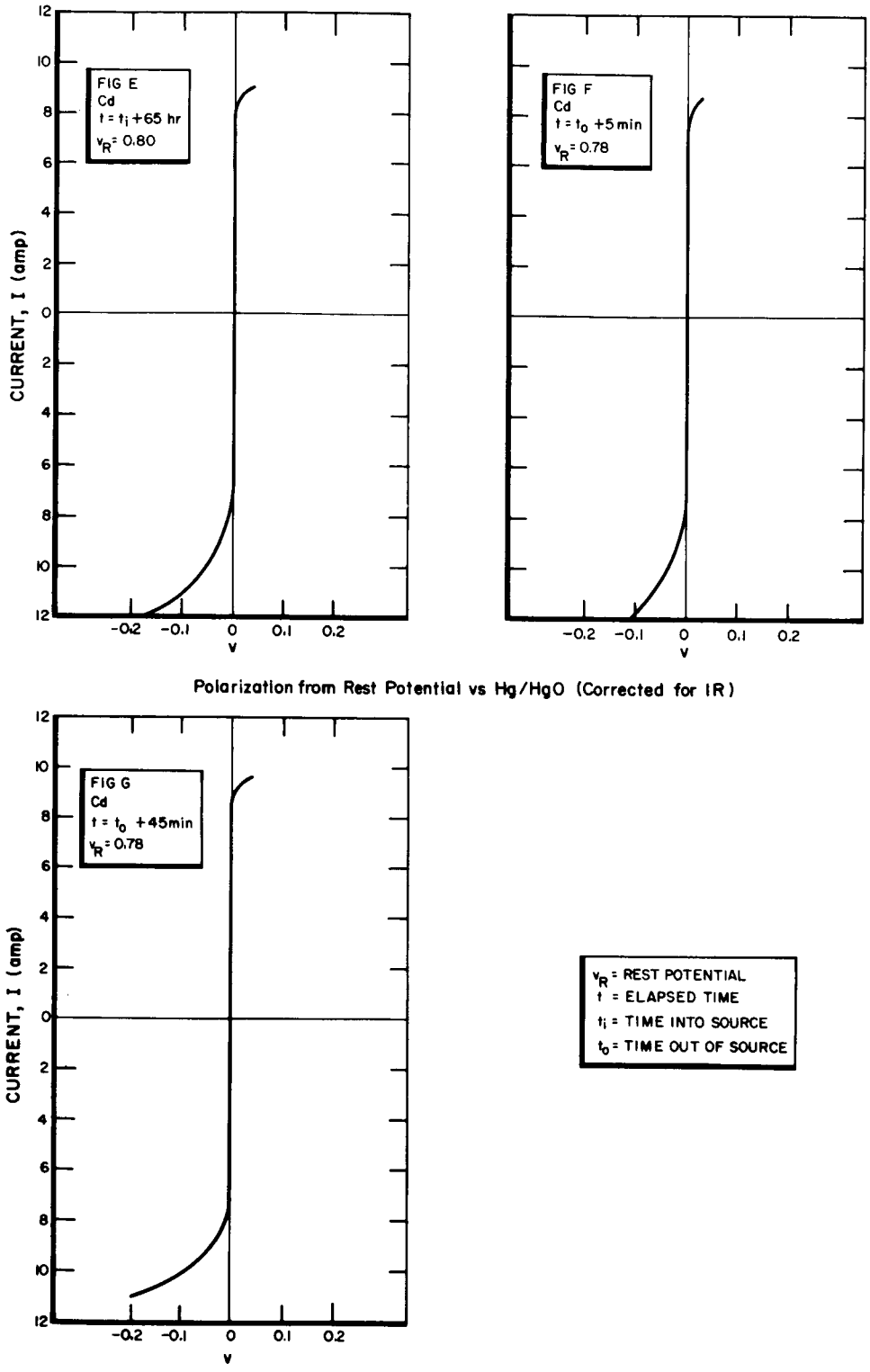

Figure 6A. Polarization of Cd Electrode

IV. DISCUSSION AND CONCLUSIONS

A. Cadmium Electrode Capacity

In the runs with the compartmented cells, used primarily for study of sloughing, the changes in cadmium electrode capacity do not follow the trend observed in the unchambered cells. The electrodes would be likely to experience a different environment in these two types of cell. In light of this, the following discussion treats only the regular (single chamber) cell results.

Cadmium electrodes at 75 per cent of full charge lose about 15 per cent of their capacity upon being irradiated to 8.9×10^7 rads (H_2O) in a Co-60 source. The data obtained at 100 per cent and at 50 per cent of charge indicate at most only a small capacity loss. In the single chamber cells, the scatter at 50 per cent state of charge is small; at 100 per cent state of charge it is quite large (Figure 3). The speculations presented previously[2] to explain the loss observed at 75 per cent of charge would seem to predict even greater loss at 50 per cent of charge and thus cannot explain the observations.

The scatter in the measured capacity data may be real and perhaps due to variations in cell manufacture rather than experimental error. A more complete investigation appears to be needed at several states of charge before an explanation for the results can be put forth.

B. Effect of State of Charge on Sloughing

As already noted, some difference in results are obtained in separated

cells as compared with the single chamber cells. With this in mind, it is noted (Table III) that at 75 and 50 per cent of charge (in separated cells) most of the sloughed material came from the cadmium electrode. This is not consistent with the conclusion reached previously with indirect evidence on single chamber cells. As only single pieces of data have been obtained for each state of charge, more data are needed to confirm this observation.

From the data in Table III some conclusions may be drawn. The Cd/Ni ratio of sloughed material in single compartment cells is higher at 100 per cent state of charge than at 50 per cent state of charge. Because of wide scatter, the results at 75 per cent state of charge are inconclusive. From data on the divided cell runs, most of the sloughed material at 50 and 75 per cent of charge came from the cadmium electrode.

This may mean, for example, that cadmium metal is easily sloughed and, since its amount decreases as the state of charge decreases, less is available to slough at lower states of charge; this is consistent with the results of x-ray analysis on sloughed material from runs A-1 and A-2 (Table III).

The amount of material lost in the blank runs at 45°C, the temperature inside the Co-60 source, seemed high. Upon analysis the Cd/Ni ratios were all nearly 1:1. Most of the material was found to be silica from the quartz liner.

C. Radiolysis of the Electrolyte

The very low "G" values for hydrogen and oxygen given in Tables IV and V suggest that at a total dose of 6.6×10^7 rads (H_2O) the process of

radiolysis of the KOH solutions is in a steady state condition; i.e., very little, if any, net formation of products is occurring. This would mean that the "G" values reported are apparent yields. To determine the initial "G" values for the radiolysis of KOH solutions, irradiations of lower total dosage should be made. This would enable the course of build-up of products to be determined, and would yield true "G" values as well as more data on the mechanism of the process.

At 30 per cent KOH the yield of O_2 and H_2 is very small. The nickel electrode affects the yield of O_2 in a striking manner as shown by the 20-fold increase in the "G" value for O_2. The radiation appears in some way to be discharging the nickel electrode, or the nickel electrode is catalyzing the decomposition of an intermediate, e.g., hydrogen peroxide. The effect of the nickel electrode on $G_{(H_2)}$ is considered negligible.

As expected, no oxygen was detected in the presence of the cadmium electrode. The large increase in $G_{(H_2)}$ due to the presence of the cadmium electrode is not surprising. This is to be expected as removal of one product will enhance the production of another. For example, reaction of cadmium metal with OH radicals would permit the formation of hydrogen gas as was shown previously[2] in the radiolysis mechanism presented.

This postulated effect of the electrodes on $G_{(H_2)}$ and $G_{(O_2)}$ would produce on them a form of self discharge. It would be of interest to leave a charged cell on open circuit in a radiation field to determine how much self discharge actually occurs.

A detailed proposed radiolysis mechanism has been previously presented.[2]

In reference to this mechanism, no O_2 or H_2 should be formed in the radiolysis in the absence of an impurity since the radicals produced ($G_H = 3.7$ and $G_{OH} = 2.7$) will destroy the molecular products ($G_{H_2} = 0.4$ and $G_{O_2} \sim 0.35$) by the reactions:

$$H + O_2 \longrightarrow HO_2 \qquad e^-_{aq} + O_2 \longrightarrow O_2^- \xrightarrow{\text{(2 steps)}} 3/4\ O_2^*$$

$$OH + H_2 \longrightarrow H_2O + H \qquad O^- + H_2 \longrightarrow e^-_{aq}$$

Neutral Solution — Basic Solution

However, a small steady state concentration of H_2 and O_2 is observed in the proper 2/1 ratio at 0.5 per cent KOH indicating some solute other than KOH must be present which reacts either with e^-_{aq} or O^- or both. This solute may be a trace impurity, especially a +2 cation, in the H_2O. The decrease in yield of H_2 and O_2 with increasing basicity suggests that the OH^- decomposition by radiation yields O^- and e^-_{aq} with $G_{(O^-)} \cong 0.1$, and that this enhanced yield of radicals further reduces the gaseous evolution. That is the mechanism:

Overall Primary Processes:

$$H_2O \xrightarrow{\gamma} H_2,\ O_2,\ e^-_{aq},\ O^-$$

$$OH^- \xrightarrow{\gamma} O^-,\ e^-_{aq}$$

Subsequent Reactions:

$$O^- + H_2 \longrightarrow e^-_{aq}$$

$$e^-_{aq} + O_2 \longrightarrow O_2^-$$

$$O_2^- + \tfrac{1}{2} H_2O \longrightarrow OH^- + 3/4\ O_2$$

*That is normally one talks of H and OH but these are now known to exist as e^-_{aq} and O^- in basic solution.

predicts

$$H_2 \text{ yield} = G_{H_2} - G_{0^-}$$

$$O_2 \text{ yield} = G_{O_2} - \tfrac{1}{4} (\text{net yield of } e^-_{aq}) = G_{O_2} - \tfrac{1}{4} \left[G\, e^-_{aq} + G_{0^-} \right]$$

The increase in yield of H_2 and O_2 at 40 per cent KOH may again be an effect of impurities in the KOH which consume the radicals and allow H_2 and O_2 production.

Reactions of radicals with H_2O_2 (or HO_2^-) should not be considered in the mechanism since H_2O_2 has not been detected in the products. Further refinements are needed in this proposed mechanism.

D. Voltammetry of Nickel and Cadmium Electrodes

Polarization effects were expected on both the cadmium and the nickel electrodes from surface coverage by the radiolysis products. The measurement made after 45 minutes in the source seemed to indicate this effect at the nickel electrode but the effect diminished during later measurements.

The effects observed on the cadmium electrode can be attributed to temperature since the polarization decreased upon entering the source while returning to normal when removed from the Co-60 radiation and 45°C environment.

V. FUTURE PLANS

Several additional runs at 100, 75 and 50 per cent of charge in single chamber cells are planned to clarify the question of capacity loss of the cadmium electrode. Irradiations at 25 per cent of charge will also be made. The question of the origin of the sloughed material will also be investigated further in compartmented cells.

If time permits, several irradiation runs on cells using electrodes from other manufacturers' batteries are planned.

VI. REFERENCES

1. AI-64-11, "The Effects of Radiation on Nickel-Cadmium Battery Electrodes. I," Final Report.

2. AI-64-161, "The Effects of Radiation on Nickel-Cadmium Battery Electrodes. II," Mid-Point Report.